

The effect of varying Fe-content on transport properties of K intercalated iron selenide $K_xFe_{2-y}Se_2$

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Abstract

We report the successful growth of high-quality single crystals of potassium intercalated iron selenide $K_xFe_{2-y}Se_2$ by Bridgeman method. The effect of iron vacancies on transport properties was investigated by electrical resistivity and magnetic susceptibility measurements. With varying iron content, the system passes from semiconducting/insulating to superconducting state. Comparing with superconductivity, the anomalous “hump” effect in the normal state resistivity is much more sensitive to the iron deficiency. The electrical resistivity exhibits a perfect metallic behavior ($R_{300K}/R_{35K} \approx 42$) for the sample with little iron vacancies. Our results suggest that the anomalous “hump” effect in the normal state resistivity may be due to the ordering process of the cation vacancies in this non-stoichiometric compound rather than magnetic/structure transition. A trace of superconductivity extending up to near 44 K was also detected in some crystals of $K_xFe_{2-y}Se_2$, which has the highest T_c of the reported iron selenides.

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The discovery of superconductivity in iron-based pnictides has attracted a great deal of research interest.[1] The PbO-type α -FeSe_x, which has an extremely simple structure with only FeSe₄ tetrahedral layers stacked along c-axis, the same as the FeAs₄ tetrahedral layers found in pnictides, was discovered subsequently at 8 K in samples prepared with Se deficiency.[2] The superconductivity of FeSe_x can be further enhanced up to 14 K by partially replacing Se with Te.[3] High pressure studies at 4.5 GPa have dramatically yielded the superconductivity at 37 K.[4] Very recently, by intercalating potassium between the FeSe layers, i.e., K_xFe₂Se₂, superconductivity has been observed up to 30 K,[5] which is the same as those in optimal doped pnictides AFe₂As₂ (A=Ca, Sr, Ba, Eu).[1] In iron pnictides, many open questions are waiting to be solved, especially the relationship between superconductivity, structural change and magnetic order. Hence, systematic investigations on the superconductivity in K_xFe₂Se₂ can provide us some hints on the difference or common features between pnictide and selenide systems, and further shed light on the mechanism of superconductivity in Fe-based superconductors.

In present work, we report the successful growth of high quality single crystals of K_xFe_{2-y}Se₂ with different Fe-deficiency using a Bridgeman method and a systematic study on effect of Fe-deficiency on the transport properties. We find that the system displays unique properties such as electrical resistivity ranging from superconducting to semiconducting/insulating, which can be tuned by adjusting the growth conditions. Comparing with superconductivity, the anomalous “hump” effect in the normal state resistivity in superconducting samples is much more sensitive to the iron deficiency. We speculate that the anomalous “hump” effect in the normal state resistivity may be due to the ordering process of the cation vacancies in this non-stoichiometric compound rather than magnetic/structure transition. Furthermore, a trace of superconductivity extending up to near 44 K was detected in some batches of K_xFe_{2-y}Se₂, which has the highest T_c of the reported iron selenides. The appropriate nominal compositions and growth conditions are important key parameters to modulate the transport properties in K_xFe_{2-y}Se₂.

All the samples were prepared by Birdgeman method. Fe_{1+y}Se was firstly synthesized as precursor by reacting Fe powder with Se powder at 750 °C for 20 hours. K pieces and Fe_{1+y}Se powder were put into an alumina crucible with nominal compositions (Hereafter, all the compositions used in this paper refer to the nominal compositions) as K_xFe_{2+y}Se₂ (0.6≤x≤ 1.0; 0≤y≤ 0.3). The alumina crucible was then sealed into Tantalum tube with

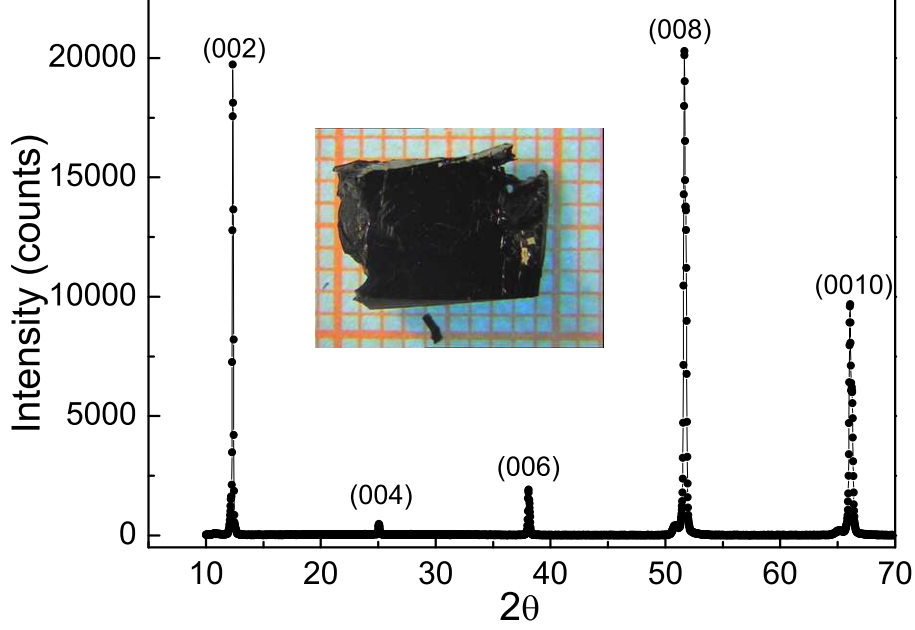


FIG. 1: (Color online) The X-ray diffraction pattern of $K_{0.8}Fe_2Se_2$ crystal with mainly the (00ℓ) reflections indicates that the crystals are cleaved along the a - b plane. Inset shows the typical photography of the grown $K_{0.8}Fe_2Se_2$ crystal.

Argon gas under the pressure of 1.5 atom, then the sealed Ta tube were vacuum sealed into quartz tubes. In some cases, the alumina crucible was directly sealed into thick walled quartz tube with Ar under the pressure of 0.4 atom. The sample was put in box/tube furnace and heated to 1050 $^{\circ}C$ slowly and held there for 2 hours, and then was cooled to 750 $^{\circ}C$ over 60~200 hours to grow the single crystals. The obtained crystals with sizes up to 8mm \times 8mm \times 5mm have the form of platelets with shinny surface. These crystals were characterized by X-ray diffraction (XRD). The elemental composition of the single crystal was checked by energy dispersive X-ray (EDX) spectroscopy analysis. The resistivity was measured by a standard 4-probe method. The DC magnetic susceptibility was measured with a magnetic field of 10 Oe. These measurements were performed down to 2 K in a Physical Property Measurement System (PPMS) of Quantum Design with the VSM option provided.

Figure 1 shows the X-ray diffraction pattern of $K_{0.8}Fe_2Se_2$ (nominal composition) with the 00ℓ ($\ell = 2n$) reflections, which is consistent with previous reports. The lattice constant $c = 14.15 \text{ \AA}$ was calculated from the higher order peaks, comparable to the result from powder diffraction.[5] The picture of grown crystal with nominal composition $K_{0.8}Fe_2Se_2$ is

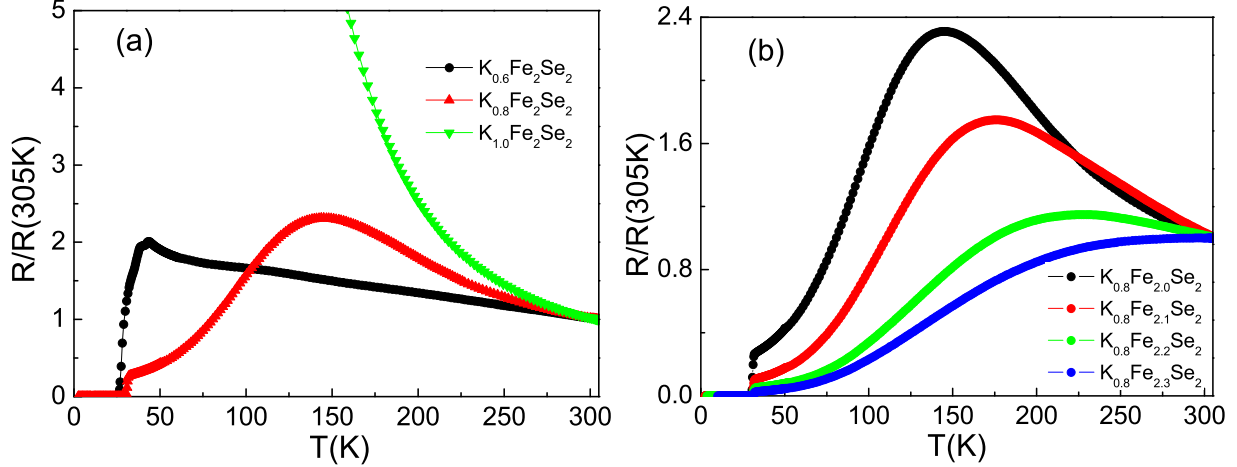


FIG. 2: (Color online) Temperature dependent resistivity of grown $K_xFe_{2+y}Se_2$ ($0.6 \leq x \leq 1.0$, $0 \leq y \leq 0.3$) crystals. Different electronic transport properties demonstrated by the resistivity curves have been observed.

presented in the inset of Fig.1.

Firstly, we investigated the relation between K concentration and the behavior of the resistivity. Figure 2a shows clearly that with the increase of nominal K doping, the system evolves from semiconductor-like (superconducting) to a typical structure same as previous report with a broad peak around 140 K, then becomes a semiconductor/insulator-like system without superconducting observed inside. The EDX data shows that as the nominal content of K was increased from 0.8 to 1.0, the iron content in the obtained single crystals systemically decreased from 1.8 to 1.5 and the superconductivity finally disappeared. This indicates that the high deficiency of Fe has a major detrimental effect on the transport properties.

Secondly, we systematically changed the concentrations of Fe ions with K fixed to study the transport behavior. Figure 2b shows the temperature dependence of resistivity for $K_xFe_{2+y}Se_2$ crystals between 2 K and 300 K. It is obvious that the behavior of the electrical transport has changed with the increase of Fe concentrations (corresponding to the decrease of Fe deficiency.) When the Fe deficiency is large, the resistivity curve possesses an obvious metal-insulator (MI) transition at around 140 K. At high temperatures, the sample shows the semiconductor-like behaviors, while below the transition temperature it presents a metallic behavior.[5] With increasing the Fe concentration, the hump diminishes gradually and the position shifts to high temperature, and finally vanishes in the sample with nominal

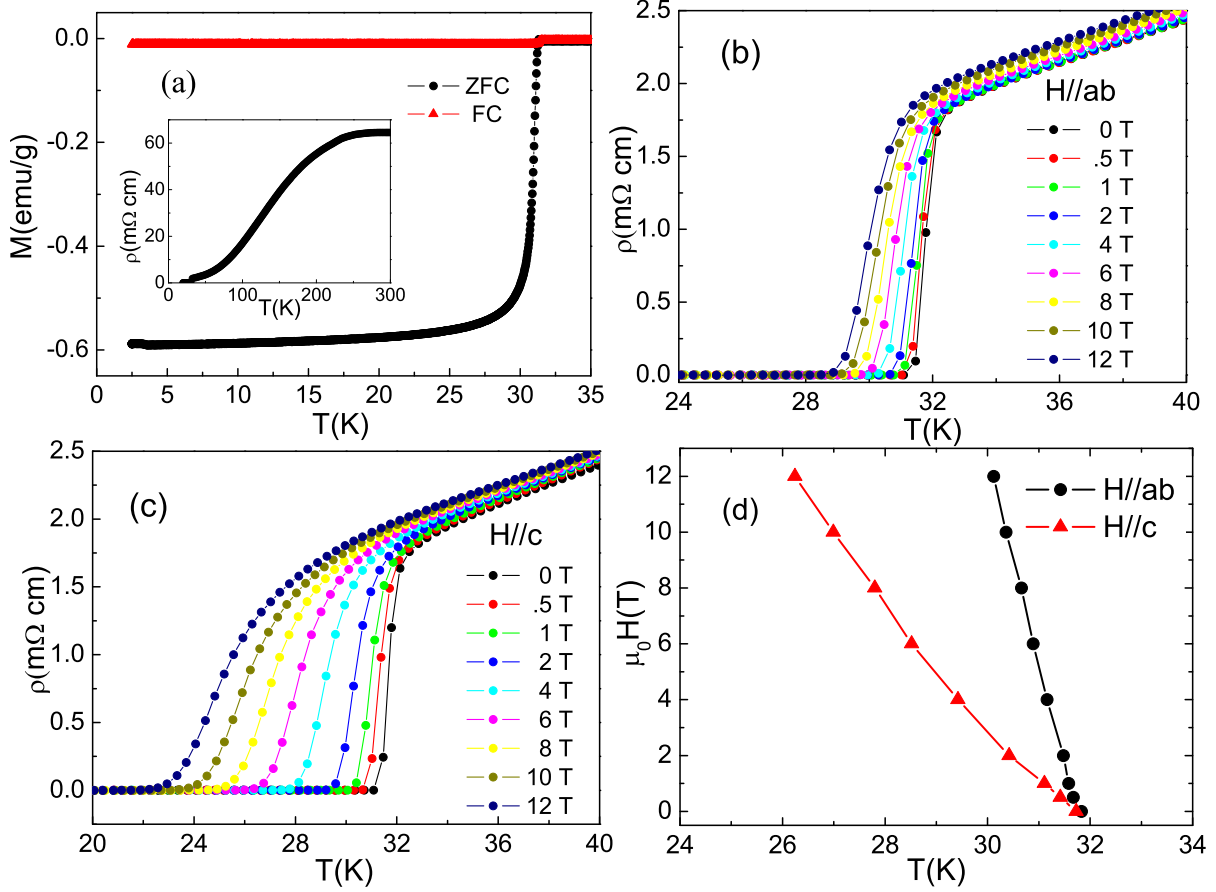


FIG. 3: (Color online) (a) DC magnetic susceptibility of $K_{0.8}Fe_{2.3}Se_2$ crystal. Inset shows the temperature dependence of resistivity between 300 K and 20 K; The temperature dependence of resistivity for $K_{0.8}Fe_{2.3}Se_2$ crystal with the applied field parallel (b) and perpendicular (c) to the ab plane; (d) Temperature dependence of $H_{c2}(T)$ for $K_{0.8}Fe_{2.3}Se_2$ crystal.

composition $K_{0.8}Fe_{2.3}Se_2$. Here the electrical resistivity exhibits a perfect metallic behavior. However, the superconducting critical temperature, T_c , increases slightly (less than 0.8 K) with decreasing Fe deficiency. We note that there is not any anomaly in the temperature dependence of magnetic susceptibility and there is also no structural phase transition occurring over the temperature ranging from 60 to 300 K.[6] The semiconductor-metal like transition may be attributed to the ordering process of the cation vacancies in the non-stoichiometric compound of $K_xFe_{2-y}Se_2$ and it significantly influences the electrical resistivity. We notice that similar issues concerning order-disorder phenomena have been discussed in the transition metal carbides and the high- T_c compounds where the ordering of the vacancies play an important role in controlling the normal-state resistivity and superconductivity.[7, 8]

Interestingly, the temperature dependence of electrical resistivity under high pressure has been investigated by Sun et al.,[6] where the “hump” was successively suppressed by applying pressure and the superconductivity was destroyed simultaneously, in contrast to the results of our study. There is no obvious correlation between the superconducting critical temperature and the broad hump.

Figure 3a presents the magnetic susceptibility as a function of the temperature from 3 K to 35 K for the sample with nominal composition $\text{K}_{0.8}\text{Fe}_{2.3}\text{Se}_2$ under the magnetic field of 10 Oe. The zero field cooling (ZFC) and field cooling (FC) susceptibility both show sharp transitions at around 32 K. From ZFC, it can be estimated that the superconducting volume fraction at 10 K is about 100%, which demonstrates the bulk superconductivity in the samples. Inset of Fig.3a shows the typical resistivity curve of $\text{K}_{0.8}\text{Fe}_{2.3}\text{Se}_2$, which clearly shows the metallic behavior with high residual resistivity ratio ($R_{300\text{K}}/R_{35\text{K}} \approx 42$).

Figure 3b and 3c show the behavior of resistivity of $\text{K}_{0.8}\text{Fe}_{2.3}\text{Se}_2$ in external magnetic field up to 12 T. In Figure 3b, the applied field is within the ab plane ($H \parallel ab$) while in Fig.3c the applied field is parallel to the c axis ($H \parallel c$). We see the superconducting transition is suppressed in both conditions but the effect of magnetic field is much larger when the field is applied along the c axis of the single crystals in stead of within the ab plane. The corresponding upper critical field H_{c2} as a function of temperature obtained from a determination of the midpoint of the resistive transition is plotted in Fig.3d. The curves are steep with

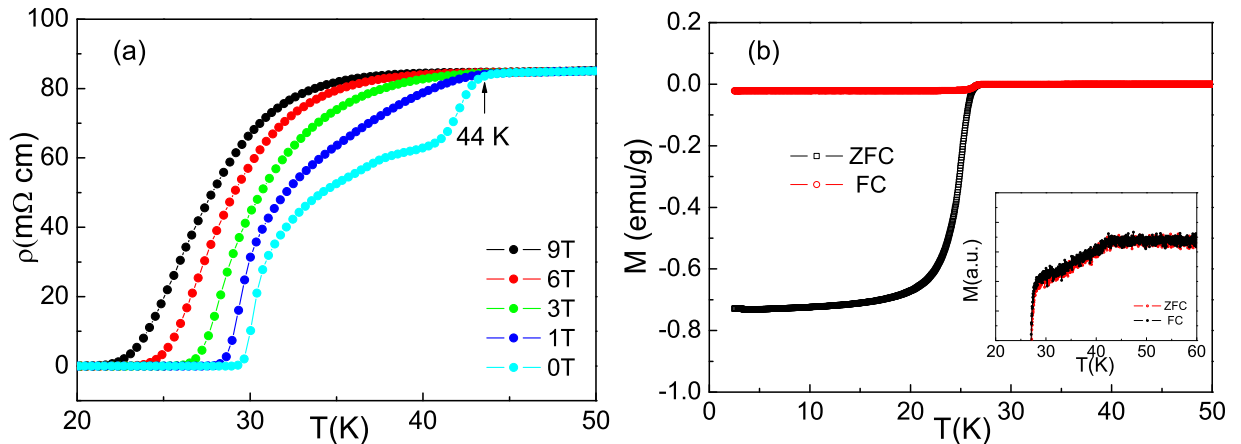


FIG. 4: (Color online) (a) Temperature dependence of the resistivity under different magnetic field; (b) Magnetic susceptibility of the same samples. Inset of figure 4b is the enlarged part from figure 4b which clearly indicates the transition around 44 K.

slopes $-dH_{c2}/dT|_{T_c}=7.20$ T/K for $H\parallel ab$ and $-dH_{c2}/dT|_{T_c}=2.17$ T/K for $H\parallel c$. According to the Werthamer-Helfand-Hohenberg (WHH) formula[9] $H_{c2}(0) = -0.69(dH_{c2}/dT)T_c$ and taking 32 K as T_c , the upper critical fields are estimated to be $H_{c2}^{ab}=159$ T and $H_{c2}^c=48$ T. The ratio of H_{c2}^{ab}/H_{c2}^c is about 3.3 which is consistent with previous reports.[10]

One issue we want to point out is that a trace of superconductivity with T_c up to 44 K has been observed in several batches of samples with nominal composition $K_{0.8}Fe_2Se_2$. Figure 4a shows the temperature dependence of the electrical resistivity in the low temperature region. It is clear that there exist two transition steps on the resistivity curve measured under zero field, one at about 38 K and another at about 44 K. To verify whether the transition at 44 K is due to superconductivity, we measured the field dependence of resistivity and observed the resistivity curves change at around 44 K, and the kink shifts to low temperature with increasing magnetic fields. Magnetic susceptibility has also been measured on the same samples and it is clearly shown in the Fig.4b that once the temperature is lower than around 44 K, the magnetization begins to decrease and the rate of decreasing greatly enhances once the temperature is lower than 28 K, which corresponds to the transition temperature of zero resistivity. Hence it raises one question: where does the superconductivity come from, “122” phase with super high quality, or other new phase? Detailed characterization of the superconducting phase is in progress.

In conclusion, we have successfully grown series of single crystals $K_xFe_{2-y}Se_2$ with different Fe vacancies. A trace of superconductivity extending up to near 44 K was also observed in some $K_xFe_{2-y}Se_2$ crystals, which has the highest T_c of the reported iron selenides. The anomalous semiconductor-metal-like transition is observed only in the sample with high level of Fe vacancies. We speculate that the anomaly is associated with the ordering of the framework vacancies, which significantly influences the electrical resistivity. The more ordered phase showing a large reduction in residual resistivity is due to reduction of electron-vacancy scattering. A more detailed study is needed in order to better understand the correlation of superconductivity and the anomalous metal-insulator transition.

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